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The Gaseous Reaction Between Hydrogen Sulphide and Sulphur Dioxide

A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY AT NEW YORK UNIVERSITY

BY

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I wish to record my indebtedness to Dr. H. Austin Taylor
under whose direction this work was undertaken.

THE GASEOUS REACTION BETWEEN HYDROGEN SULPHIDE AND SULPHUR DIOXIDE

BY W. ANDREW WESLEY[1]

The most important problem which confronts the physical chemist today is the determination of the mechanism of chemical reaction. The interaction of solids is relatively unimportant and the behavior of substances in solution seems in most cases to be highly complex. Therefore great interest attaches to the study of gaseous reactions and the elucidation of their mechanisms.

The rapidity with which hydrogen sulphide and sulphur dioxide react in aqueous solution and the fact that even the most reactive substances become inert upon complete desiccation[2] suggested that reaction may proceed at a much slower rate, if at all, between the dry gases. Although it has been known for at least a century that hydrogen sulphide does react with sulphur dioxide according to the equation:

$$2H_2S + SO_2 = 3S + 2H_2O$$

nothing definite was known of the manner in which these gases combine in the absence of a liquid phase except that the end products are sulphur and water. The work herein discussed is a study of the kinetics of the reaction, data of which are most valuable in deciding the mechanism of the reaction. The results indicate clearly that the gases are brought into an active condition by adsorption on the walls of the reaction tube, and combine to a very small extent, if at all, in the gaseous phase.

The demonstration of the rapid reaction between hydrogen sulphide and sulphur dioxide in the presence of excess moisture was a common lecture experiment as early as 1812, but it is not known by whom this reaction was first observed. However, Cluzel[3] noted at that time that no combination would result if the gases were first dried by passing over calcium chloride. Many investigators[4] have studied the reaction in a more or less qualitative way, but their results throw little light on the gaseous reaction because they permitted water to condense in the reaction system.

The equilibrium in the reaction has been recently studied in California. Lewis and Randall[5] were unable to use the method of determining equilibrium by rapidly cooling the reacting substances and analyzing, because the reaction occurs "rapidly in either direction according to the conditions imposed."

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Baker: J. Chem. Soc., **65**, 623 (1894); Mellor and Russel: **81**, 1272 (1902).

[3] Ann. Chim. Phys., **84**, 162 (1812).

[4] Mulder: Jahresb., **1856**, 86; Corenwinder: Compt. rend., **53**, 140 (1861); Gripon: **56**, 137 (1863); Meyers: J. prakt. Chem., **108**, 123 (1869); Compt. rend., **74**, 195 (1872).

[5] J. Am. Chem. Soc., **40**, 362 (1918).

They were obliged to use a static manometric method with an excess of liquid sulphur present and were able to work only at one temperature, namely 445°C. Since the change in pressure occurring at this temperature is very small the results, which show an average deviation from the mean of 26 per cent may be regarded as quite satisfactory. Randall and Bichowsky[1] investigated the equilibrium in this system at temperatures above 880°C., where appreciable amounts of hydrogen are present at equilibrium. On the first page of their paper a brief footnote makes the following statement: "A mixture of moist SO_2 and H_2S when passed through a clean glass tube at 60°, deposited but little sulphur. However, when the tube was etched, sulphur was deposited rapidly at the same temperature." This is the only indication in the literature of the true nature of the reaction.

Experiment

The kinetics of the reaction were studied by a dynamic method. The work of Lewis, Randall and Bichowsky demonstrated the difficulty of applying static methods to this system. The gases were allowed to flow at a constant rate through a reaction chamber kept at constant temperature. Determinations of the composition of the gases leaving the chamber permitted the calculation of the rate at which reaction was proceeding. The temperature coefficient was determined through a range of temperatures for two reaction chambers, equal in volume, but of widely different surface area. The effect of variation of partial pressures of the reacting gases was then determined at constant temperature.

Hydrogen sulphide of 99.5 per cent purity can be readily prepared from calcium sulphide as recommended by Pollitzer.[2] Kahlbaum's chemically pure calcium sulphide in lump form was used in an ordinary Kipp generator with a solution of hydrochloric acid. Before connecting the generator to the remainder of the apparatus about four liters of H_2S were drawn off to ensure the removal of all air. The gas then generated was completely absorbable in 20 per cent sodium hydroxide.

The sulphur dioxide was taken from a cylinder of commercial liquid SO_2 Half of the original contents had been withdrawn, thus removing any air present. Each gas was passed over phosphorus pentoxide before entering the reaction chamber.

In order to obtain accurate measure of the rate of flow of a gas by means of a flow-meter a very steady pressure must be maintained. For this purpose a second Kipp generator containing distilled water was connected to the first and used as a gasometer. A three-way stopcock was used at the mouth of the gasometer so that it could be permanently connected with both the generator and the hydrogen sulphide flow-meter. Since the gasometer contained water it also served to remove all traces of hydrogen chloride carried over from the

[1] J. Am. Chem. Soc., **40**, 368 (1918).

[2] Z. anorg. Chem., **64**, 121 (1909).

generator. The sulphur dioxide gasometer contained concentrated sulphuric acid and was similarly connected with the cylinder of liquid sulphur dioxide and the sulphur dioxide flow meter.

The flow-meters were of the type described by Benton[1] for very small rates of flow. The capillaries were about one centimeter in length, blown in Pyrex. Distilled water was used in the manometers and was of course saturated with the gas passing through the flow-meter.

From its flow-meter each gas was passed through a large Pyrex U-tube containing phosphorus pentoxide. These drying tubes were sealed directly to the remainder of the apparatus which was entirely of Pyrex. From the drying tube each gas was passed through a stopcock lubricated with metaphosphoric acid. The gases were then mixed and passed directly into the reaction tube. A coil of Pyrex tubing of five millimeters bore joined to a test tube furnished the first reaction tube, which had a volume of 56 cc. and an inner surface area of approximately 320 sq. cm. Reaction tube 2 was blown from two test tubes giving a resultant volume of 51 cc. and surface area of 120 sq. cm.

The reaction tube was maintained at constant temperature in an electric furnace whose inside dimensions were 15 cm. in length by 7 cm. in diameter. The top of the furnace was well insulated with an asbestos board 1.5 cm. in thickness through which the glass tubes connected with the reaction tube and also the thermocouple wires were passed. The current through the furnace windings was controlled by a small rheostat. The temperature was measured by a Hoskins pyrometer, the thermocouple being cemented to the furnace cover so that it occupied the same position in the furnace in each experiment.

The success of this method of determining the extent of reaction depends mainly upon the manner of treatment of the gases coming from the reaction tube. In general, rapid cooling is necessary in order to prevent further reaction but with the system under discussion the gases flowing from the reaction tube cannot be cooled to room temperature. The reason for this is one which all previous investigators failed to observe. If but one droplet of water be allowed to condense in the presence of hydrogen sulphide and sulphur dioxide these gases proceed to react very rapidly in the solution thus formed. Their interaction results in the production of sulphur and more water. However, it was found that cooling to 100°C. effectively stopped the reaction, permitted the complete condensation of the sulphur vapor formed in the reaction tube, and prevented the condensation of moisture. A bulb about 5 cc. in volume was blown in the exit tube at the point at which it projected from the furnace covering. Here the condensed sulphur was permitted to collect. A Pyrex tube 8 cm. in length was sealed to the bulb and was ground at the end to fit the mouth of an absorption bulb. The sulphur bulb and its tube were surrounded by a housing of sheet asbestos which enclosed a 100 watt electric light bulb. The temperature of the enclosure was thus regulated between 100° and 110°C. using a rheostat in series with the lamp.

[1] J. Ind. Eng. Chem., **11**, 623 (1919).

The absorption tube was designed to obtain complete absorption without bubbling. Any type of bulb permitting even slight fluctuations in pressure caused by bubbling of the gases through the absorbing liquid rendered the manometer readings of the flow-meters uncertain. Two closed cylindrical bulbs of 1 cm. diameter and 6 cc. volume were connected at one end by a short piece of small tubing so that they were parallel and 1 cm. apart. At the other end one bulb carried a short open tube of 2 mm. bore, while the other bulb terminated in a tube ground to fit the exit of the main train of apparatus and bent so that the absorption bulbs assumed a horizontal position when connected to the exit. In this position a large surface of absorbing liquid was exposed to the gases entering the bulb, and since they dissolve rapidly and completely in that solution, no bubbling could take place.

Each flow-meter was calibrated by absorbing, in 30 per cent sodium hydroxide solution, all the gas passing through it during a definite time interval at various readings of the manometer. The time interval was made long enough to give an increase in weight of the absorption bulb of from 0.15 to 0.2 g. A calibration curve for each flow-meter was made by plotting difference in manometer levels against grams of gas per minute. These curves were checked once a week at several different rates of flow.

The reaction tube was cleaned with a chromic acid cleaning solution and washed well with distilled water. After it was placed in the furnace and sealed to the remainder of the apparatus it was dried at 500°C. with a slow stream of dry sulphur dioxide over-night. This procedure was also of the nature of a heat treatment, since comparable reaction velocities could not be obtained with a fresh tube. It was further found necessary to allow the reaction to proceed for eight or nine hours within the tube before its condition became fixed and duplicate results could be obtained.

The next step was to bring the furnace to the desired temperature at which it was maintained by manual operation of the furnace rheostat within $\pm 1°$ throughout the run. The rate of flow of gases was kept constant by frequent manipulation of stop-cocks. After attaching the weighed absorption bulb in order to make a run, the stop-cocks were not touched since it was found that greater accuracy was achieved by averaging the initial and final readings of the flow-meter manometers during the run. For each run there were recorded initial and final values of the following: time, temperature, the two manometer levels in each flow-meter and the weight of the absorption bulb.

In experiments 1 and 2 at all temperatures below 580°C. the rate of reaction showed a gradual change with time for a period of from 2 to 3 hours. Only when a constant rate of formation of sulphur had finally been reached and several runs differed no more than one per cent from the mean, was the experiment at this temperature discontinued.

The results of experiments 1 and 2 show that the reaction takes place almost entirely on the surface of the reaction tube. Therefore experiment 3 was performed at constant temperature with constant total volume of gas entering the reaction tube but with various partial pressures of hydrogen sulphide and sulphur dioxide.

Calculations and Results

The rate at which H_2S and SO_2 entered the reaction tube was obtained from the average manometer readings by reference to the calibration curves where rates were plotted in grams per minute. A portion of the gas mixture reacted to produce sulphur, which condensed out completely in the sulphur bulb, and water which passed on into the absorption bulb. The increase in weight of the latter is therefore equal to the weight of unchanged H_2S and SO_2 plus that of the water formed. The difference between the total weight of H_2S plus SO_2 which entered the reaction chamber during a run and the increase in weight of the absorption bulb represents the amount of sulphur formed. If this difference be divided by the duration of the run the rate of formation of sulphur is obtained in grams per minute.

It was found in experiment 3 that the rate of the reaction as represented by the rate of formation of sulphur depends upon the partial pressures of the reactants according to the following equation:

$$K = \frac{S}{P_{H_2S}^{1.5} \quad P_{SO_2}}$$

where K is the velocity constant, S is the number of grams of sulphur formed per minute, P_{H_2S} is the average partial pressure of the hydrogen sulphide and P_{SO_2} that of the sulphur dioxide.

In order to calculate the average partial pressure of each reactant it is necessary to determine both the initial partial pressures and those after reaction has taken place to the extent necessary to form S grams of sulphur per minute. The latter calculation is complicated by the dissociation of the molecules of sulphur vapor into S_8, S_6, and S_2 molecules. The excellent work of Preuner and Schupp[1] on the dissociation of sulphur vapor furnishes the data necessary to compute the average molecular weight of sulphur vapor at various temperatures and at partial pressures between 0 and 180 mm. The latter limit is high enough to include the range of partial pressures produced under the conditions of the experiments being described. These average values were plotted against the corresponding temperatures. This afforded a means of interpolation to intermediate temperatures. Fortunately the error involved in estimating the vapor density of sulphur decreases as the temperature is increased and it is at the higher temperatures only that the volume of sulphur produced becomes large.

The partial pressures of the constituents of a mixture of gases vary but little with change in temperature. It was convenient therefore, to reduce all calculations of partial pressure to normal temperature and pressure, taking care however, to use the value for the molecular weight of sulphur vapor corresponding to the temperature of the experiment.

The data obtained in experiment 2 at 621°C. are the basis of the following computations:

[1] Z. physik. Chem., 68, 129 (1910).

Experimental Data

Temp.	Time	Wt. H_2S/min.	Wt. SO_2/min.	Wt. absorbed
621°C.	10 min.	0.01105g.	0.01049 g.	0.1317 g.

Computations

Total Wt. reactants = $0.02154 \times 10 = 0.2154$ g.
Total Wt. sulphur = $0.2154 - 0.1317 = 0.0837$ g.
Wt. sulphur per min. = S = 0.00837 g.
Hereafter all volumes are per minute.

$$\text{Vol. } H_2S = \frac{\text{Wt. } H_2S \text{ per min.} \times 1000}{\text{Wt. Liter } H_2S} = \frac{.01105 \times 1000}{1.5392} = 7.179 \text{ cc.}$$

$$\text{Vol. } SO_2 = \frac{\text{Wt. } SO_2 \text{ per min.} \times 1000}{\text{Wt. Liter } SO_2} = \frac{.01049 \times 1000}{2.9267} = 3.584 \text{ cc.}$$

Total Vol. reactants = 10.763 cc.
Initial $P_{H_2S} = 0.667$ atmos.
Initial $P_{SO_2} = 1 - P_{H_2S} = 0.333$ atmos.

$$\text{Vol. } H_2S \text{ reacted} = S \times \frac{2 \text{ Mol. Wt. } H_2S}{3 \text{ At. Wt. S}} \times \frac{1000}{\text{Wt. Liter } H_2S}$$

$$= 3.854 \text{ cc.}$$

Therefore Final Vol. $H_2S = 7.179 - 3.854 = 3.325$ cc.
Similarly Final Vol. $SO_2 = 1.679$ cc.

$$\text{Vol. S formed} = \frac{S \times 22400}{\text{Mo. Wt. S at } 621^\circ} = 2.678 \text{ cc.}$$

Vol. H_2O formed = 3.899 cc.
Final Total Vol. = Final Vol. $H_2S + SO_2 + S + H_2O$
= 11.581 cc.
Hence Final $P_{H_2S} = 0.287$ atmos.
Final $P_{SO_2} = 0.145$ atmos.

$$\text{Average } P_{H_2S} = \frac{\text{Initial} + \text{Final}}{2} = 0.477 \text{ atmos.}$$

Average $P_{SO_2} = 0.239$ atmos.
$P_{H_2S}^{1.5} = (0.477)^{1.5} = 0.330$

$$\text{Hence } K = \frac{S}{P_{H_2S}^{1.5} \times P_{SO_2}} = 0.1061$$

Results

G = Increase in weight of absorption bulb.
S = Number of grams of sulphur formed per minute.
P_{H_2S} = Average partial pressure of H_2S
P_{SO_2} = Average partial pressure of SO_2
K = Velocity Constant = $S/(P_{H_2S}^{1.5} \times P_{SO_2})$
T = Absolute Temperature

Experiment 1

Reaction tube 1. Volume 56 cc. Surface area 317 sq. cm.

	Temp. °C	Time Min.	Grams H_2S / Min.	Grams SO_2 / Min.	G	$S \times 10^5$
1.	371	10	0.01097	0.01033	0.1885	245
2.	406	10	0.01093	0.01029	0.1705	417
3.	430	10	0.01120	0.01038	0.1623	535
4.	452	10	0.01092	0.01055	0.1501	646
5.	471	10	0.01110	0.01043	0.1418	735
6.	475	10	0.01116	0.01044	0.1400	760
7.	510	10	0.01111	0.01045	0.1252	904
8.	539	10.9	0.01100	0.01046	0.1293	960
9.	571	10	0.01107	0.01031	0.1149	989

	Mol. Wt. Sulphur	$P^{1.5}_{H_2S}$	P_{SO_2}	$K \times 10^4$	log K	$1/T \times 10^4$
1.	203	0.493	0.309	160	−1.796	15.53
2.	180	.451	.291	318	−1.498	14.73
3.	165	.429	.277	450	−1.347	14.22
4.	152	.389	.273	608	−1.216	13.79
5.	140	.375	.257	762	−1.118	13.44
6.	137	.370	.254	809	−1.092	13.37
7.	116	.333	.238	1139	−0.943	12.77
8.	100	.312	.231	1331	−0.876	12.32
9.	85	.301	.222	1481	−0.829	11.85

Experiment 2

Reaction tube 2. Volume 51 cc. Surface area 121 sq. cm.

	Temp. °C	Time Min.	H_2S / Min.	SO_2 / Min.	G	$S \times 10^5$
10.	438	10	0.01108	0.01026	0.1905	229
11.	484	10	.01101	.01033	.1754	380
12.	521	13	.01101	.01054	.2077	557
13.	550	10	.01094	.01044	.1487	651
14.	583	10	.01100	.01040	.1376	764
15.	621	10	.01105	.01049	.1317	837
16.	666	10	.01100	.01025	.1203	922
17.	688	10	.01098	.01038	.1173	963
18.	725	10	.01100	.01032	.1088	1044
19.	733	10	.01111	.01041	.1091	1061

EXPERIMENT 2 (Continued)

	Mol. Wt. Sulphur	$P^{1.5}_{H_2S}$	P_{SO_2}	K × 10⁴	log K	1/T × 10⁴
10.	160	0.497	0.306	151	−1.821	14.06
11.	131	.457	.292	285	−1.545	13.21
12.	110	.406	.277	495	−1.305	12.59
13.	95	.379	.264	650	−1.187	12.15
14.	80	.350	.248	880	−1.055	11.68
15.	70	.330	.239	1061	−0.974	11.19
16.	66	.312	.225	1313	−0.882	10.65
17.	66	.301	.224	1429	−0.845	10.41
18.	65	.285	.213	1720	−0.765	10.02
19.	65	.284	.213	1754	−0.756	9.69

EXPERIMENT 3

Reaction Tube 2. Volume 51 cc. Surface area 121 sq. cm.
Temperature 480°C.

Molecular weight of Sulphur for partial pressures from 0 to 100 mm. = 124.

TABLE I

	Time Min.	Grams H_2S / Min.	Grams SO_2 / Min.	G	S × 10⁵	P_{H_2S}	P_{SO}
21.	10	0.01335	0.00587	0.1585	337	0.744	0.153
22.	10	.01335	.00610	.1591	354	.735	.157
23.	10	.01270	.00733	.1617	386	.689	.193
24.	12	.01276	.00744	.1943	401	.685	.194
25.	10	.01172	.00918	.1674	416	.625	.249
26.	10	.01175	.00925	.1666	434	.619	.149
27.	10	.01065	.01078	.1700	443	.561	.302
28.	10	.01072	.01084	.1690	466	.557	.300
29.	10	.00964	.01320	.1821	463	.486	.368
30.	11	.00961	.01323	.2014	453	.486	.375
31.	12	.00953	.01328	.2201	447	.485	.379
32.	10	.00851	.01544	.1970	425	.424	.447
33.	10	.00636	.01939	.2232	343	.313	.584
34.	11	.00635	.01933	.2471	354	.310	.582
35.	10	.00639	.01937	.2215	361	.310	.581

TABLE II

$$K_1 = \frac{S}{P^2_{H_2S}\ P_{SO_2}} \qquad K_2 = \frac{S}{P_{H_2S}\ P^{0.5}_{SO_2}} \qquad K_3 = \frac{S}{P^{1.6}_{H_2S}\ P_{SO_2}}$$

$$K = \frac{S}{P^{1.5}_{H_2S}\ P_{SO_2}} \qquad K_4 = \frac{S}{P_{H_2S}\ P^{0.78}_{SO_2}} \qquad K_5 = \frac{S}{P_{H_2S}\ P_{SO_2}}$$

$10^4 \times$	K_1	K_2	K_3	K	K_4	K_5
21.	398	116	353	343	196	296
22.	417	125	369	357	204	307
23.	421	128	363	350	202	290
24.	441	133	379	365	211	302
25.	428	133	355	338	219	267
26.	455	141	376	358	205	282
27.	466	143	369	349	201	262
28.	501	153	396	373	214	279
29.	533	157	417	371	208	259
30.	511	153	384	356	200	249
31.	501	149	376	349	196	243
32.	529	140	376	344	188	224
33.	599	144	377	336	167	188
34.	633	149	395	351	174	196
35.	647	153	405	359	178	200
Average	499	141	379	353	196	256
Average Deviation	12.4%	6.8%	3.7%	2.5%	12.4%	12.4%

Errors.

Lewis and Randall[1] determined the equilibrium constant at 445°C. for the reaction

$$2H_2S + SO_2 = 3S(l) + 2H_2O + Q \text{ calories}$$

at constant partial pressure of sulphur to be

$$K_P = \frac{P^2_{H_2O}\ P^{0.5}_{S_6}}{P^2_{H_2S}\ P_{SO_2}} = 649$$

The variation of K_P with temperature depends upon Q in accordance with the van't Hoff isochore

$$\frac{d \ln K_P}{d T} = \frac{-Q}{R T^2}$$

To prove that the above K_P is less than that at all temperatures below 445° it is only necessary to show that Q is positive. The following heats of formation are given by Lewis:

[1] Lewis and Randall: "Thermodynamics" (1923).

$3S(l)$ from $3S$(rhombic) $= -1401$ calories
$2H_2O(g)$ from $O_2(g)$ and $2H_2(g) = 105640$ calories
$2H_2S$ from S(rhombic) and $2H_2(g) = 9520$ calories
SO_2 from S(rhombic) and $O_2(g) = 69000$ calories

The value of Q is therefore $105640 - 1401 - 9520 - 69000$, that is, 25719 calories. Below 445° the amount of S_2 in the vapor phase is negligible and the exponent of P_S varies from about $\frac{1}{2}$ to about 3/8.

Not only does the value of K_P increase as the temperature is lowered, but the saturation value of P_S rapidly diminishes. These facts indicate that the product $P^2_{H_2S} P_{SO_2}$ at equilibrium must diminish very rapidly with decrease in temperature. Since each of the partial pressure values in the equilibrium equation is less than one atmosphere, the product $P^2_{H_2O} P^n_S$ is always much less than one. Therefore the product $P^2_{H_2S} P_{SO_2}$ must always be much less than $1/K_P = 0.00154$. Under the conditions of the experiment the value of $P^2_{H_2S} P_{SO_2}$ in the exit gases was in no case less than 0.003.

This result proves that it is impossible for the sulphur condensing at the exit of the reaction chamber to react with the water vapor in the exit gases.

The sulphur bulb was maintained at a temperature of between 100° and 110°C. The vapor pressure of sulphur at 110°C. is 0.0136 mm.[1] The molecular weight of sulphur vapor at 110°C. is 256. The weight of 1 cc. is therefore 0.00083 g. The most rapid rate at which the gases entered the absorption bulb was 14.7 cc. per minute. The weight of sulphur carried into the absorption bulb per minute was therefore $0.0136/760 \times 14.7 \times 0.00083 = 0.000002$ g. The total weight per run of ten minutes duration was 0.00002 g.

The solubility of hydrogen sulphide in liquid sulphur reported by Pélabon[2] introduced no appreciable error. The amount dissolved increases with rise in temperature and even at 440°C. is but 0.3 cc. = 0.00045 g. per gram of sulphur. At most only 0.1 g. of sulphur was formed during a run.

The fact that the reaction took place mainly on the surface of the reaction tube eliminates the possibility of the introduction of error due to reaction during the cooling of the gases from the temperature of the reaction tube to that of the sulphur bulb. The amount of surface in the exit tube whose temperature lay between that of the reaction tube and 110° was certainly less than 6 sq. cm. With reaction tube 1 whose surface was about 317 sq. cm. no measurable reaction took place at 180°C. It was also found that the condensation of sulphur in the sulphur bulb had no measurable effect upon the reaction velocity.

There seem, therefore, to be no inherent errors, so that the accuracy of the results depends upon the errors made in measurement and calculation. A consideration of the errors in the measurement of time, temperature, weight of gas absorbed and rate of flow of reactants showed that the precision was such as would lead to an average deviation of 2.5 per cent in the value of K, the velocity constant.

[1] Gruener: J. Am. Chem. Soc., **29**, 1396 (1907).
[2] Compt. rend., **124**, 35 (1897).

Discussion of Results

1. *The Heterogeneity of the Reaction.*

The results of experiments 1 and 2 are given graphically in Fig. 1. The values of log $_{10}$K are plotted as abscissae against the corresponding values of 1/T as ordinates. At 435°C., where $1/T = 14.12 \times 10^{-4}$, log K for the reaction tube 1 is -1.315 and for tube 2 is -1.850. Therefore the reaction proceeded 3.4 times as fast in tube 1 as in tube 2. At 571° this ratio becomes 1.9. In the mean the reaction occurred 2.7 times as fast in tube 1 as in tube 2. The ratio of their surface areas was 317 to 121 or 2.6. This proportionality

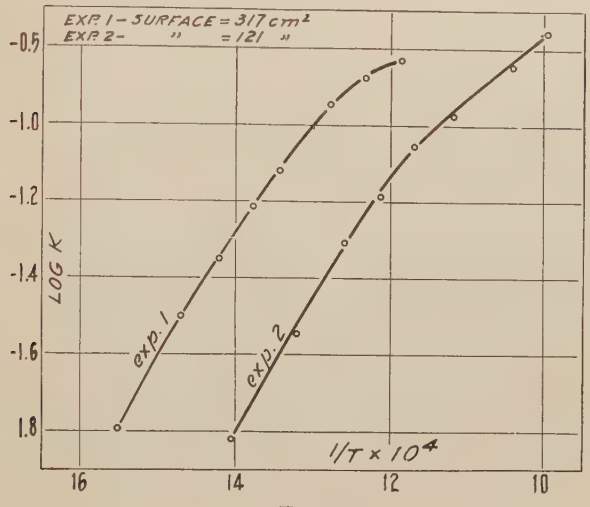

Fig. 1

of reaction velocity to surface is definite evidence that there can be little reaction between H_2S and SO_2 in the gas phase. The volumes of the two tubes were almost equal at 56 and 51 cc. respectively.

2. *The Temperature Coefficient.*

The variation of the velocity constant of a chemical reaction with temperature may be expressed by the Arrhenius equation: $d \ln K/d T = E/RT^2$ or in the integrated form:

$$\log K_2/K_1 = E/4.57(1/T_1 - 1/T_2)$$

When T_1 and T_2 are temperatures 10° apart, the value of K_2/K_1 is called the temperature coefficient of the reaction velocity. The values so calculated are given in the following table:

	Experiment 1		Experiment 2	
Temp. °C	Temp. Coef.	E Cal./Mol.	Temp. Coef.	E Cal./Mol.
370	1.239	17600	——	——
400	1.169	14000	——	——
435	1.151	14000	1.170	15600
475	1.134	14000	1.151	15600
510	1.076	8900	1.137	15600
550	1.037	4900	1.093	11900
600	——	——	1.058	8500
680	——	——	1.045	8000

The values of E thus calculated are probably not equal to the actual heats of activation of the chemical reaction involved. The amounts of reacting substances adsorbed on the surface of the vessel and therefore actually participating in the reaction, undoubtedly decrease with a rise in temperature. This would make the apparent value of E, calculated from the observed temperature coefficient, smaller than the true value which measures the actual stability of the adsorbed molecule.

It can be seen that the temperature coefficient decreases with increase in temperature. At lower temperatures it is comparatively high, then decreases steadily. This variation is in accord with the theory that the reaction velocity depends upon the amount of reactants adsorbed, the resultant temperature coefficient being equal to the sum of the negative temperature coefficient of adsorption and the positive coefficient of the chemical reaction. There are no data available which show the heats of adsorption of SO_2 and H_2S on glass at high temperatures. The magnitude of the effect of temperature on the adsorption of these gases cannot be estimated, so that the true heat of activation for the reaction between H_2S and SO_2 on glass surfaces cannot yet be calculated.

The fact that the temperature coefficients of the reaction were different at a given temperature for the two reaction vessels used is probably due to a slight difference in the surfaces. It may be that only the SiO_2 groups of the surface are active in adsorption of H_2S or SO_2, or that only the Na_2O groups can activate these gases. Again it may be that each of these groups activates one of the reactants. Further study of the adsorptions may determine the exact details of the mechanism at the surface. It is remarkable indeed, in view if the recent work of Hinshelwood on the decomposition of formic acid[1], that the curves of log K against 1/T are so nearly parallel. Hinshelwood found that the velocity of the decomposition of formic acid and the relative ease with which it follows the two alternative paths of reaction to form $H_2 + CO_2$ or $H_2O + CO$ are very sensitive to the nature of the glass surface. At 300°C. for example, the amounts of $CO_2 + H_2$ in the products of formic acid decomposition on equal surface areas were:

[1] Proc. Roy. Soc., **100** A, 575 (1922); J. Chem. Soc., **121**, 1668 (1922); **123**, 1014, 1333 (1923).

Duro glass	74%	73%	63%
Soda glass	19.1%	18.3%	16.5%

Duro glass is similar in composition to pyrex glass.

3. *Mechanism of the Reaction.*

Examination of the results tabulated for experiment 3 shows immediately that the rate of formation of sulphur is directly proportional to some power of the partial pressure of each of the reactant gases. This suggests that both gases are adsorbed and only adsorbed molecules react. If but one of the gases is adsorbed and reaction takes place when a molecule of the other gas collides with an adsorbed molecule, there is a range of pressures through which the reaction velocity is independent of the partial pressure of the adsorbed type of gas. In this range the surface of the catalyst is saturated with adsorbed gas and the velocity depends upon the number of molecules of the unadsorbed type which strike the surface. At constant temperature, the rate at which the molecules of a given gas strike a plane surface is directly proportional to the pressure of the gas. Langmuir[1] found that at high temperatures the surface of platinum in a mixture of carbon monoxide and oxygen is nearly covered with oxygen, and the velocity is then limited by the rate at which the monoxide strikes the surface.

If both the gases are adsorbed and only one is activated by the adsorption, the reaction velocity will be directly proportional to the fraction of surface covered by the activated gas, and inversely proportional to the fraction of surface covered by the inert gas. The results obtained by Bodenstein and Ohlmer[2] on the oxidation of carbon monoxide on quartz, in which case the adsorbed carbon monoxide is inert, and the results of Bodenstein and Fink[3] on the oxidation of sulphur dioxide, in which case the adsorbed SO_3 is inert, indicate just such a mechanism.

The results of experiment 3 are best explained by assuming that both the H_2S and SO_2 are adsorbed and that reaction takes place only between these adsorbed molecules. If this is indeed the case, then the reaction velocity would be proportional to the fraction of surface covered by groups consisting of one SO_2 and two H_2S molecules situated adjacently. The probability of this condition occurring is proportional to the product of the square of the fraction of surface covered by H_2S times the fraction of surface covered by SO_2. Let F_{H_2S} equal the fraction of surface covered by H_2S and F_{SO_2} the fraction covered by SO_2 molecules. Then the velocity will be given by:

$$S = k F_{H_2S}^2 F_{SO_2}$$

The fraction of surface covered by an adsorbed gas is given by the Freundlich isotherm:

$$F = a P^{1/n}$$

[1] Trans. Faraday Soc., **17**, 621 (1921).
[2] Z. physik. Chem., **53**, 175 (1905).
[3] Z. physik. Chem., **60**, 1 (1907).

Therefore, $$F_{H_2S} = k_1 P_{H_2S}^{1/n}$$

$$F_{SO_2} = k_2 P_{SO_2}^{1/m}$$

Substituting, $$S = K P_{H_2S}^{2/n} P_{SO_2}^{1/m}$$

The adsorption of H_2S on glass surfaces has not yet been studied. Therefore the value of 1/n is not known. Bangham and Burt[1] have studied the adsorption of SO_2 on glass quite recently but their research "brought to light a conspicuous difference in the behavior of SO_2 from that of any gas previously tested" (N_2O, NH_3 and CO_2). Continued heating in vacuo at 200°C. did not remove all the adsorbed SO_2 so that they were unable to evaluate the pressure exponent. However, McGavack and Patrick[2] found that for SO_2 adsorbed by silica gel the value of 1/m is 0.485 at 30°C., 0.533 at 57°, 0.662 at 80° and 0.745 at 100°C. If these values be extrapolated it will be seen that the value of 1/m approaches 1 asymptotically at about 150°C. It seems reasonable therefore, to conclude that the value in the above expression at temperatures above 350°C. is nearly 1.

The value of 2/n must lie somewhere between 2 and 0. Various exponents for P_{H_2S} lying in this range were used in calculating velocity constants and the results are tabulated in experiment 3, Table II. It will be seen that the smallest average deviation is obtained where 2/n = 1.5. This indicates that the pressure exponent for hydrogen sulphide at 480°C. is about 0.75. At high temperatures the pressure exponents of adsorption vary but slowly with temperature.

Very few data have yet been determined on reactions at catalyst surfaces where both reactants are adsorbed and activated. None are available for any reaction of the same type as the one studied, where the reaction is apparently trimolecular and both gases activated by adsorption. Pease[3] found that the velocity of combination of ethylene and hydrogen at copper surfaces could be expressed by an equation

$$K = \frac{dP/dt}{V_{H_2}^{0.80} \; V_{C_2H_4}^{0.66}}$$

where dP/dt = rate of decrease of pressure

V_{H_2} = initial volume of hydrogen

$V_{C_2H_4}$ = initial volume of ethylene.

The mechanism of this reaction is quite similar to the H_2S-SO_2 reaction but it is bimolecular and hence simpler.

Summary

1. Measurements have been made of the velocity of combination of hydrogen sulphide and sulphur dioxide in Pyrex reaction tubes at temperatures ranging from 370 to 730°C. The velocity was found to be proportional to the surface area of the reaction chamber, which proves that the glass surface

[1] J. Phys. Chem., **29**, 548 (1925).

[2] J. Am. Chem. Soc., **42**, 946 (1920).

[3] J. Am. Chem. Soc., **45**, 2235 (1923).

acts as a contact catalyst for the reaction. Further the temperature coefficient was found to decrease with a rise in temperature.

2. Measurements of the velocity at constant temperature show it to vary directly as the partial pressure of the sulphur dioxide and as the partial pressure of the hydrogen sulphide raised to the 1.5 power.

3. A mechanism of reaction in harmony with the modern theories of heterogeneous reactions has been suggested, and substantiated by the results. According to this mechanism each of the reactants is activated by adsorption on the surface of the glass and reaction then follows between the activated molecules only.

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